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<p>(21) International Application Number: PCT/US98/16198</p> <p>(22) International Filing Date: 4 August 1998 (04.08.98)</p> <p>(30) Priority Data: 08/906,141 5 August 1997 (05.08.97) US</p> <p>(71) Applicant: SC JOHNSON COMMERCIAL MARKETS, INC. [US/US]; 8310 16th Street, P.O. Box 902, Sturtevant, WI 53177-0902 (US).</p> <p>(72) Inventors: CAMPBELL, J., David; 713 Silent Sunday Court, Racine, WI 53402 (US). KAAI, Michihiro; Toyoake-shi, 1187-81, Tsurune Magome-cho, Toyoake-shi 470-11 (JP). SCHATZ, David, D.; 2931 Washington Avenue, Racine, WI 53405 (US). TEYMOUR, Fouad; 1825 West Palm Drive, Mt. Prospect, IL 60056 (US).</p> <p>(74) Agents: RYMARZ, Renee, J. et al.; SC Johnson Commercial Markets, Inc., Patent Section, 8310 16th Street M/S 510, Sturtevant, WI 53177-0902 (US).</p>	<p>(81) Designated States: AU, CA, CN, JP, KR, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>Without international search report and to be republished upon receipt of that report.</i></p>	
<p>(54) Title: PROCESS FOR THE PREPARATION OF MACROMERS</p>		
<p>(57) Abstract</p> <p>A process is disclosed for preparing low molecular weight homomacromers and comacromers. The process of preparing a homomacromer comprises the steps of: (a) charging a reactor with (i) a single ethylenically unsaturated monomer selected from the group consisting of acrylic monomers or monoalkenyl aromatic monomers and (ii) if said ethylenically unsaturated monomer is not a thermally initiating monomer, a free radical polymerizable initiator, to form a polymerizable reaction charge; and (b) heating the reaction charge during continuous mixing in the reactor to a reaction temperature in the range from about 180 °C to about 500 °C for a residence time greater than 5 minutes to form the low molecular weight homomacromers, provided that if the residence time is 60 minutes or less that the reaction temperature is greater than 270 °C. The comacromers are prepared by charging the reactor with (i) at least two ethylenically unsaturated monomers selected from the group consisting of acrylic monomers, monoalkenyl aromatic monomers or mixtures thereof and (ii) if at least one of said ethylenically unsaturated monomers is not a thermally initiating monomer, a free radical polymerization initiator, and heating the reactor to a reactor temperature in the range from about 180 °C to about 500 °C for a residence time greater than 5 minutes to form the low molecular weight comacromers, provided that if the residence time is 60 minutes or less that the reaction temperature is greater than 270 °C and further provided that if the reaction charge is a mixture of acrylic monomer and monoalkenyl monomer and the residence time is 60 minutes or less then the reaction temperature is greater than 310 °C.</p>		

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PROCESS FOR THE PREPARATION OF MACROMERS

BACKGROUND OF THE INVENTION

TECHNICAL FIELD

- 5 This invention relates to a process for polymerization of monoalkenyl aromatic monomers and/or acrylic monomers at temperatures and residence times that produce low molecular weight homomacromers or comacromers having terminal unsaturation.

BACKGROUND ART

- 10 Polymerization of ethylenically unsaturated monomers at moderate temperatures to produce low molecular weight polymers is known in the art. U.S. Patent No. 4,529,787 describes a process for polymerizing mixtures of monoalkenyl aromatic monomers and acrylic monomers in the temperature range from 180°C to 270°C, with a residence time from 2-60 minutes. The same temperature range is employed in the method described in U.S. Patent
- 15 No. 4,546,160 for polymerization of mixtures containing only acrylic monomers. In this reference, the residence time varies from 1-30 minutes. Both of temperatures above 270°C leads to adverse effects on the products, for example, discoloration, oxidation, depolymerization, and side reactions.
- 20 The methods of the aforementioned references employ free radical polymerization initiators. This is typical of most known methods for production of low molecular weight polymers. For example, monoethylenically unsaturated carboxylic acids, such as acrylic acid, may be converted to low molecular weight polymers in aqueous solution in the presence of an initiator, as described in U.S. Patent No. 5,268,437. This method employs temperatures in
- 25 the range from 130°C to 240°C. Another method for production of low molecular weight acrylic and hydroxyl-containing polymers is described in U.S. Patent No. 4,600,755. This method requires use of aqueous hydrogen peroxide as an initiator at temperatures above 140°C. Copper salts are used as initiators for production of low molecular weight polymers of monoethylenically unsaturated carboxylic acids and esters in U.S. Patent No. 5,100,980.
- 30 The production of low molecular weight oligomers using cobalt chain transfer agents is also well known. For example, U.S. Patent No. 4,680,352 describes the use of Co(II) chain transfer agents to control the molecular weight of free radical polymerization of acrylic

and/or styrene monomers. The preparation of macromers that are both copolymers and homopolymers using specific cobalt (II) chelates as catalytic chain transfer agents is described in U.S. Patent No. 5,028,677. Suitable reaction temperatures are said to be between about 50°C and 150°C. The preparation of terminally unsaturated monomers using
5 such cobalt-containing chelate transfer agents is described in U.S. Patent No. 5,587,431. The process temperatures are said to range from room temperature to 200°C or higher, but preferably between about 40°C and 100°C. U.S. Patent No. 5,324,879 describes the preparation of oligomers using cobalt (III) chain transfer agents and exemplifies reaction temperatures between 60°C and 95°C.

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Other types of chain transfer agents have also been employed. Japanese Patent Publication No. 62-232408 describes the preparation of an acrylic polymer having a functional group on one terminal by heating a mixture of an acrylic monomer, a functional group chain transfer agent and a polymerization initiator to about 75°C in an inert atmosphere followed by
15 addition to a corresponding polymerization system to form a polymer having a number average molecular weight of 1000 to 30,000. Macromers prepared using ω -unsaturated oligomer as a chain transfer agent are described in U.S. Patent No. 5,362,826. Reaction temperatures of 20°C to 200°C are said to be suitable.

20 Other various techniques for preparing macromers have also been employed. Japanese Patent Publication No. 60-133007 describes the preparation of a macromer obtained by reacting a polymer containing a carboxyl group derived from mercaptopropionic acid at one end and a glycidyl group-containing monomer in the presence of a catalyst. Macromers prepared with a monomer unit having an $-\text{SO}_3\text{M}$ functional group, wherein M is alkali metal
25 or ammonium, are described in Japanese Patent Publication No. 05-247117, Japanese Patent Publication No. 04-119526 and Japanese Patent Publication No. 05-287010. A macromer containing a carboxyl group in the main chain and a vinyl-polymerizable functional group solely on the chain terminal end is described in Japanese Patent Publication No. 01-268,709. U.S. Patent No. 5,147,952 is directed to the preparation of macromers by anionic
30 polymerization of methacrylic acid ester monomer using a specific polymerization initiator.

Thermally-initiated polymerization, in which a free-radical polymerization process is initiated by heating rather than by addition of initiators, has been used to prepare low molecular weight polymers from ethylenically unsaturated monomers. U.S. Patent No. 4,414,370 describes a thermally-initiated polymerization process for preparing low
5 molecular weight polymers in a continuous reactor, at temperatures from 235°C to 310°C, with a residence time of at least 2 minutes. This reference suggests that polymerization at temperatures above 310°C leads to adverse effects on the products, for example, discoloration, oxidation, depolymerization, and side reactions. Copolymerization of monoalkenyl aromatic monomers with acrylic monomers are disclosed. However,
10 polymerization of either type of monomer alone under these conditions is not exemplified.

Higher temperatures are employed in the polymerization process described in European Patent Application EP 687,690. This reference describes the use of a temperature range of 250°C to 500°C for polymerization of acrylic acid in the presence of at least one initiator,
15 with optional addition of other acrylate monomers or monoalkenyl aromatic monomers, to produce low molecular weight polymers with terminal unsaturation, also referred to as macromers. However, the residence time is limited to the range from 0.1 seconds to 5 minutes. Polymerizations at these temperatures for longer residence times are said to be undesirable because the yield of terminally unsaturated oligomers will be decreased without
20 substantially affecting molecular weight or monomer conversion to polymer.

A process for polymerization of acrylic monomers and/or monoalkenyl aromatic monomers at high temperatures or long residence times which provide low molecular weight homomacromers and polymacromers having terminal unsaturation would be highly
25 desirable.

SUMMARY DISCLOSURE OF THE INVENTION

This invention is directed to a process for preparing low molecular weight macromers, i.e., homomacromers and comacromers, having terminal unsaturation.

30 In one embodiment, homomacromers are prepared by the process comprising the steps of
(a) charging a reactor with (i) a single ethylenically unsaturated monomer selected from the

group consisting of acrylic monomers or monoalkenyl aromatic monomers and (ii) if said ethylenically unsaturated monomer is not a thermally initiating monomer, a free radical polymerization initiator, to form a polymerizable reaction charge; and (b) heating the reaction charge during continuous mixing in the reactor to a reaction temperature in the
5 range from about 180°C to about 500°C for a residence time greater than 5 minutes to form the low molecular weight homomacromers, provided that if the residence time is 60 minutes or less that the reaction temperature is greater than 270°C.

Yet another embodiment is directed to the preparation of comacromers by (a) charging a
10 reactor with (i) at least two ethylenically unsaturated monomers selected from the group consisting of acrylic monomers, monoalkenyl aromatic monomers or mixtures thereof and (ii) if at least one of said ethylenically unsaturated monomers is not a thermally initiating monomer, a free radical polymerization initiator, to form a polymerizable reaction charge; and (b) heating the reaction charge during continuous mixing in the reactor to a reaction
15 temperature in the range from about 180°C to about 500°C for a residence time greater than 5 minutes to form the low molecular weight comacromers, provided that if the residence time is 60 minutes or less that the reaction temperature is greater than 270°C and further provided that if the reaction charge is a mixture of acrylic monomer and monoalkenyl monomer and the residence time is 60 minutes or less then the reaction temperature is
20 greater than 310°C. Preferably the reaction temperature of the process of this invention is greater than 270°C, more preferably greater than 310°C.

The macromers prepared by the process of this invention, are terminally unsaturated, and thus are useful, for example, as monomers in additional polymerization reactions. The
25 polymers that result from such additional polymerization reactions are useful in adhesives, coating compositions and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram showing a reactor and support equipment that may be employed in the process of this invention.

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Figure 2 is a schematic diagram showing yet another reactor and support equipment for use

in the process of this invention.

BEST MODE FOR CARRYING OUT THE INVENTION

The method of this invention produces macromers, which are polymers with terminal ethylenic unsaturation. These macromers may be homomacromers or comacromers. The term "homomacromer" describes a homopolymer having a terminal double bond, while the term "comacromer" describes a copolymer having a terminal double bond. These macromers may be characterized by parameters well known to those skilled in the art: number average molecular weight (M_n), weight average molecular weight (M_w), polydispersity (PD), and double bonds per chain (DB/chain). PD is defined in the conventional way as M_w/M_n . DB/chain is defined in terms of the double bond equivalent weight DBEQ (iodine number) as M_n/DBEQ . Number average polymerization degree (P_n) is calculated by dividing M_n by the molecular weight of the monomer.

The macromers prepared by the process of this invention generally have an M_n in a range from about 300 to about 5000, most preferably about 300 to about 1500. The DB/chain of the macromers prepared by the process of this invention typically have a value in a range from about 0.3 to about 1.2, preferably about 0.7 to about 1, most preferably about 1.

The term "acrylic monomer" as employed herein encompasses, for example, acrylates and methacrylates which include respectively, acrylic or methacrylic acid, and esters, salts, derivatives, and mixtures thereof. Examples of suitable acrylic monomers include, but are not limited to acrylic acid, methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, n-decyl acrylate, 2-hydroxyethyl acrylate, methacrylic acid, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate, tert-butyl methacrylate, n-amyl methacrylate, isoamyl methacrylate, n-hexyl methacrylate, 2-ethylhexyl methacrylate, benzyl methacrylate, 2-n-butoxyethyl methacrylate, 2-chloroethyl methacrylate, allyl methacrylate, cyclohexyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, acrylamide, N-ethylacrylamide, N,N-diethylacrylamide, methacrylamide, N-methylmethacrylamide, N-ethylmethacrylamide, N,N-

- dimethylmethacrylamide, N,N-diethylmethacrylamide, 3-chloro-2-hydroxy-propylacrylate, 2-hydroxy-butyl acrylate, 6-hydroxyhexyl acrylate, 2-hydroxymethyl methacrylate, 2-hydroxypropyl methacrylate, 6-hydroxyhexyl methacrylate, 5,6-dihydroxyhexyl methacrylate, methyl- α -chloroacrylate, methyl 2-cyanoacrylate, N-ethylacrylamide,
- 5 N,N-diethylacrylamide, t-butylaminoethyl methacrylate, 2-sulfoethyl methacrylate, trifluoroethyl methacrylate, 2-ethylbutyl methacrylate, cinnamyl methacrylate, cyclopentyl methacrylate, 2-ethoxyethyl methacrylate, furfuryl methacrylate, hexafluoroisopropyl methacrylate, 3-methoxybutyl methacrylate, 2-methoxybutyl methacrylate, 2-nitro-2-methylpropyl methacrylate, n-octyl methacrylate, 2-phenoxyethyl methacrylate, 2-
- 10 phenylethyl methacrylate, phenyl methacrylate, propargyl methacrylate, tetrahydrofurfuryl methacrylate, tetrahydropyranyl methacrylate acrylonitrile and the like. Preferred acrylate and methacrylate monomers include butyl acrylate, hexyl acrylate, acrylic acid, methacrylic acid, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, isopropyl acrylate and the like.
- 15 The acrylic monomer can also include acrylates or methacrylates containing cross-linkable functional groups, such as hydroxy, carboxyl, amino, cross-linkable isocyanate, glycidyl, epoxy, allyl, and the like. Such functional groups may be introduced to the macromers prepared by the process of this invention by the use of such functional monomers or by post reacting a macromer with techniques well known to those skilled in the art, e.g.,
- 20 esterification or transesterification.

The term "monoalkenyl aromatic monomer" as employed herein includes aromatic compounds substituted by a single alkenyl group. Examples of suitable monoalkenyl aromatic monomers include, but are not limited to styrene, α -methylstyrene, vinyltoluene, tert-butylstyrene, 2-chlorostyrene, para-methylstyrene and the like. Preferred monoalkenyl

25 aromatic monomers are styrene and α -methylstyrene.

The term "ethylenically unsaturated monomer" as employed herein includes monoalkenyl aromatic monomers and acrylic monomers. If desired during preparation of a comonomer,

30 other types of monomers that have ethylenic unsaturation may be included in the reaction mixture. For example, vinyl acetate, vinyl pyridine, vinyl pyrrolidone, methyl crotonate,

crotonic acid and maleic anhydride.

Typically, the ethylenically unsaturated monomer, or mixture of monomers is present in the reaction charge at a level of from about 60 to about 100% by weight, most preferably about
5 90 to about 100% by weight of the reaction charge. The remainder of the reaction charge may include, for example, solvents and, if necessary, initiators.

In the preparation of a comacromer, the monoalkenyl aromatic monomers and acrylic monomers may be mixed in any ratio that provides the desired properties sought in the
10 resulting macromer. When mixed, the weight ratio of monoalkenyl aromatic monomers to acrylic monomers is generally in the range of about 0.001:100 to about 100:0.001, preferably about 1:100 to about 100:1.

The process of this invention employs either relatively high reaction temperatures or long
15 residence times to obtain macromers having terminal unsaturation. Generally, the longer the residence time the lower the reaction temperature may be.

For a homomacromer, if the reaction temperature is between about 180°C to about 270°C, the residence time is greater than 60 minutes, preferably in a range between about 60 to
20 about 120 minutes. If the reaction temperature used to prepare a homomacromer is greater than 270°C the residence time is greater than 5 minutes, preferably in a range between about 10 to about 45 minutes. A particularly preferred reaction temperature range for the preparation of a homomacromer is between about 275°C to about 500°C, more preferably between about 300°C to about 400°C and most preferably between about 315°C to about
25 350°C.

In the preparation of a comacromer, if the reaction temperature is between 180°C and 270°C then the residence time is greater than 60 minutes, preferably greater than 75 minutes and most preferably in a range between about 75 to about 180 minutes. If the reaction
30 temperature used to prepare comacromer is greater than 270°C then the residence time is greater than 5 minutes preferably in a range of about 10 to 45 minutes, with the exception

that if the reaction charge is a mixture of an acrylic monomer and a monoalkenyl monomer then the reaction temperature must be greater than 310°C if the residence time is 60 minutes or less. A particularly preferred reaction temperature range for the preparation of comacromers is between about 315°C to about 500°C, more preferably between about 5 315°C to about 400°C, and most preferably between about 315°C to about 350°C.

Without being bound to theory, it is believed that the high reaction temperatures and/or long residence times employed in the method of this invention favor polymer chain β -scission reactions over chain termination reactions. In the case of β -scission reactions, a terminally 10 ethylenically unsaturated polymer results. Termination reactions do not result in production of reactive terminal double bonds. Thus, high temperatures or longer residence times favor production of polymers with terminal double bonds, and a value for DB/chain that is near 1.

For reaction mixtures containing monoalkenyl aromatic monomers, i.e., thermally initiating 15 monomers, the reaction is generally carried out in the substantial absence of polymerization initiators. It is believed that the absence of initiators also favors production of double bonds over chain termination. However, in certain embodiments of this invention it may be desirable to employ polymerization initiators, particularly when the level of thermally initiating monomers, such as styrene, are relatively low in the reaction mixture. The 20 initiators suitable for carrying out the process of this invention are compounds which decompose thermally into radicals. Suitable initiators preferably have half-life periods in the radical decomposition process from about 1 hour to about 10 hours in the temperature range from about 90°C to about 100°C. Others with about 10 hour half-lives at temperatures significantly lower than 100°C may also be used. Suitable initiators are, for 25 example, aliphatic azo compounds such as 1-tert-amylazo-1-cyanocyclohexane, azo-bis-isobutyronitrile, and 1-tert-butylazocyanocyclohexane and peroxides and hydroperoxides, such as tert-butylperoctoate, tert-butylperbenzoate, dicumyl peroxide, di-tert-butyl peroxide (DTBP), tert-butyl hydroperoxide (TBHP), cumene hydroperoxide, and the like. The initiator is preferably added simultaneously with the monomers. For this purpose, it is 30 either mixed with the monomer feed or added to the process as a separate feed. If used, the initiator is typically present in an amount in a range of about 0% to about 10% by weight of

the monomer mixture.

If desired, from about 0 to 40 percent and preferably from about 0 to 10 percent reaction solvent may be employed in the polymerization process of this invention. The solvent, when employed, may be added to the reactor prior to the addition of the monomer feed, or simultaneously with the ethylenically unsaturated monomer feed or added to the reactor as a separate feed. The selection of the particular solvent and its level of addition may be made based on the monomers employed, the ultimate use for the prepared macromer as well as to assist in controlling the reaction parameters.

Most conventional polymerization or reaction solvents may be utilized in the present process to prepare the low molecular weight polymers of the instant invention. The solvent employed should be selected to ensure that the solvent system is compatible with the monomer or monomers used under the reaction conditions, i.e., the solvent should impart adequate solvency to avoid substantial polymer precipitation. The higher boiling solvents may be used due to their low pressure at high temperature. Examples of such higher boiling solvents include the aromatic alcohols, such as benzyl alcohol, the toluene alcohols and the like; the alcohol and glycol ethers, esters and mixed ethers and esters, such as diethylene glycol, "Cellosolve" (registered trademark of the Union Carbide Corporation, Danbury, Connecticut) (ethylene glycol monoethyl ether), butyl Cellosolve (ethylene glycol monobutyl ether), Cellosolve acetate (ethylene glycol monoethyl ether acetate), "Carbitol" (registered trademark of the Union Carbide Corporation) (diethylene glycol monoethyl ether), the glymes, e.g., ethylene glycol dimethyl ether, and the diglymes, e.g., "Diglyme" (registered trademark of I.C.I. (England) London, England) (diglycol methyl ether), and the like.

The aliphatic alcohols, such as for example, isopropanol, butanol, hexanol and decanol, can also be used. Further, various hydrocarbon fractions may be utilized with the most preferred being Solvesso 150 or Solvesso 100 (a registered trademark of the Humble Oil and Refining Company.) Aromatic solvents can also be employed, for example, toluene, xylene, cumene, and ethyl benzene.

Preferably, no solvents are employed. However, if used, the solvent choice will be dependent on the monomer composition and can be readily determined without undue experimentation.

- 5 Other components that may be employed in the reaction mixture, but which are not necessary and which may be substantially absent, include (i) chain transfer agents, (ii) other polymers or (iii) other macromers. The use of such additional components is well known to those skilled in the art and thus elaboration thereon is not deemed necessary.
- 10 The process of this invention is intended to be carried out in a reactor in which continuous mixing can be achieved. Suitable reactors include those in which thorough mixing of the reactor contents occurs. Examples of suitable reactors are the continuous stirred tank reactor (CSTR), the continuous loop reactor, and a tube reactor, e.g., a plug-flow reactor. In addition, continuous mixing can be achieved using a semibatch reactor in which monomer
- 15 is fed to the reactor over a period of time. Other possible continuous reactor configurations include multiple CSTRs, a CSTR combined with a tube reactor, multiple loop reactors and a loop reactor in combination with a tube reactor. The desired mixing in a tube reactor may be achieved using a static mixer, e.g., complex baffles or by extrusion means. If a CSTR is employed, the reactor is typically provided with at least one vaned agitator driven by an
- 20 external power source, such as a motor, capable of mixing the reactor contents. The reactor is also provided with a means for controlling the temperature of the reactor contents, e.g., a reactor jacket in which a heating/cooling fluid circulates, controlled by a suitable temperature controller.
- 25 The pressure of the reactor contents typically varies from about 25 psig (172 kPag) to about 1000 psig (6895 kPag). Preferably, the pressure of the reactor contents is in the range from about 50 psig (344 kPag) to about 600 psig (4137 kPag), and most preferably from about 50 (344 kPag) psig to about 300 psig (2068 kPag).
- 30 An exemplary reactor with support equipment that may be used in this invention is shown in Figure 1. The 500 ml jacketed, stainless steel, continuous stirred tank reactor (CSTR) 2

may be initially filled with solvent used to remove the product of the previous run.

Monomer is fed into the CSTR from monomer feed tank 1 via piping 11, feed pump 30, and piping 12. The monomer feed is typically maintained at ambient temperature, although the feed could be heated or cooled to heat transfer if desired. Generally it will be desirable to

5 heat the feed since the reaction mixture or charge will be heated, although the temperature to which the feed is heated should be controlled to avoid premature polymerization. The monomer feed preferably enters the reaction mixture below the surface and in the vicinity of a magnetic drive agitator through a tube with an outside diameter of about 1/16 inch (0.16 cm). Preferably, a small flow of nitrogen is maintained on the agitator shaft to prevent

10 polymer from migrating up the shaft. Hot oil circulates through the CSTR jacket to provide temperature control, exiting via piping 13, hot oil pump 31, piping 14, hot oil furnace 3, and piping 15. Temperature controller 41 monitors the temperatures of the reactor contents and the reactor jacket, and operates control valve 51 so as to maintain a predetermined reaction temperature by dividing flow of the heated oil through piping 16 and 19, and through piping

15 17, cooler 4, and piping 18 and 19 into the CSTR jacket. A portion of the reaction mixture exits the reactor from the top through piping 20, passing through control valve 52, which is operated by pressure controller 42 so as to maintain a predetermined pressure in the CSTR. Control valve 53 is operated to divert a small portion of the flow through piping 21 for sampling. If desired, the process may employ a sampling tank 5 that is maintained under

20 vacuum by pulling a vacuum through condenser 6 which has an outlet to tank 7 for collection of the distillate formed in the condenser 6. The combined weight of the macromer collected in tank 5 and the distillate collected in tank 7 may be used to calculate a total mass balance on the system.

25 Yet another reactor with support equipment that may be used in this invention is shown in Figure 2. The 300 ml electrically-heated continuous stirred tank reactor (CSTR) 2 may be initially filled with solvent used to remove the product of the previous run. In this reactor system, monomer is fed into the CSTR from monomer feed tank 1 via piping 11, control valve 50, piping 12, feed pump 30, and piping 14. The monomer feed enters the reaction

30 mixture below the surface and in the vicinity of a magnetic drive agitator through a tube with an outside diameter of about 1/16 inch (0.16 cm). Preferably, a small flow of nitrogen

is maintained on the agitator shaft to prevent polymer from migrating up the shaft. A portion of the reaction mixture exits the reactor from the top through piping 15, passing through control valve 51, which is operated by pressure controller 40 so as to maintain a predetermined pressure in the CSTR. Product leaving control valve 51 enters storage tank 4
5 via piping 16. Piping sections 15 and 16 are heated to facilitate transfer of product.

While several embodiments of continuous stirred tank reactor systems have been described above for use in the process of this invention, this is in no way limiting as to the variations of polymerization reactor systems that may be employed. For example, variations, such as
10 reactant feed sequences, reactor size and temperature control means, which are well known to those skilled in the art can be readily employed in the process of this invention.

The examples which follow are intended as illustrations of certain preferred embodiments of the invention, and no limitation of the invention is implied.

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EXAMPLE 1

Preparation of Styrene Homomacromers

Effects of Residence Time and Temperature

Styrene (100%) was polymerized at various temperatures using the equipment described in
20 Figure 1. The reactor was operated with various average reactor residence times. For each example, the reactor was filled with Carbitol, which had been used for cleaning in the previous run, and heated to the reaction temperature. The monomer feed was then fed to the reactor at a flow rate necessary to obtain the desired residence time, and the temperature allowed to come to a steady state. The process was kept at a steady state condition for at
25 least 4 residence times before sampling. The residence time, number average molecular weight (M_n), the weight average molecular weight (M_w), and the DB/chain are displayed in Tables 1, 2, and 3 for reactions run at 288°C, 316°C, and 343°C, respectively. M_n and M_w were determined by gel permeation chromatography using a high performance liquid chromatograph (PE Nelson GPC/SEC Data System in combination with a Waters 410
30 Differential Refractometer, a Waters 510 HPLC pump and two Polymer Labs Plgel 10 μ m mixed bed 300 x 7.5 mm size exclusion columns). DBEQ was measured via an alkene

assay by Wij's titration, in which excess ICl in acetic acid and excess KI were added to a sample of the macromer, and the excess iodine was back-titrated with Na_2SO_3 . DB/chain was then calculated from M_n and DBEQ.

Table 1
288°C, 0% initiator

Example	Res. Time (minutes)	M _n	M _w	DB/chain
1A	30	1060	1831	0.555
1B	60	872	1411	0.655
1C	90	718	1086	1.052

Table 2
316°C, 0% initiator

5

Example	Res. Time (minutes)	M _n	M _w	DB/chain
1D	10	873	1365	0.882
1E	15	763	1108	0.858
1F	30	614	802	0.628
1G	60	535	659	0.633

Table 3
343°C, 0% initiator

Example	Res. Time (minutes)	M _n	M _w	DB/chain
1H	10	532	658	0.953
1I	15	478	563	0.745
1J	30	431	484	0.477
1K	60	399	440	0.341

Comparison of data from all three tables shows that the values of both M_n and M_w decrease with increasing temperature at the same residence time. Data in each table show that the values of both M_n and M_w decrease with increasing residence time. At 288°C, DB/chain increases with residence time, rising to 1.052 at a residence time of 90 minutes. In contrast, at 316°C and 343°C, DB/chain decreases with increasing residence time.

EXAMPLE 2

Preparation of a Styrene

Homomacromer With Initiator (DTBP)

Styrene was polymerized at 316°C in the equipment shown in Figure 1. Varying levels of DTBP (di-tert-butyl peroxide) were added along with the styrene as a polymerization initiator. The reactor was operated with a 15 minute average reactor residence time. The process was kept at a steady state condition for at least 4 residence times before sampling. The DTBP level, the number average molecular weight (M_n), the weight average molecular weight (M_w), and the DB/chain are set forth in Table 4.

Table 4

316°C, 15 minute residence time

Example	Styrene (% w/w)	DTBP (% w/w)	M_n	M_w	DB/chain
2A	100	0.0	733.6	1077	0.91
2B	99.5	0.5	696.6	989.4	0.816
2C	99.0	1.0	685.7	955.4	0.908

These data show that addition of DTBP tended to decrease both M_n and M_w . The effect of initiator is complex. Without being bound to theory, it is believed that when the initiator is added to styrene, which is thermally initiating, the conversion of styrene is increased (thus reducing the concentration of styrene) and thereby lowering the thermal initiation of styrene. As a result, while it is believed that generally an increase in initiator would be expected to lower the DB/chain value because of increased termination, this may not always result when an initiator is added to a system containing a thermal initiator such as styrene.

EXAMPLE 3

Preparation of a Styrene

Homomacromer with Initiator (TBHP)

Styrene was polymerized at 343°C in the equipment shown in Figure 1. Varying levels of TBHP (tertiary butyl hydroperoxide) were added along with the styrene as a polymerization initiator. The reactor was operated with a 15 minute average reactor residence time. The process was kept at a steady state condition for at least 4 residence times before sampling. The TBHP level, the number average molecular weight (M_n), the weight average molecular weight (M_w), and the DB/chain are set forth in Table 5.

Table 5

343°C, 15 minute residence time

Example	Styrene (% w/w)	TBHP (% w/w)	M_n	M_w	DB/chain
3A	100	0.0	484.7	595.9	0.775
3B	99.5	0.5	471.2	558.2	0.765
3C	99.0	1.0	470.4	556	0.743
3D	98.0	2.0	463	544.3	0.728

These data show a slight decrease in both M_n and M_w with increasing TBHP, similar to that observed for DTBP in Example 2. However, DB/chain shows a steady decrease with TBHP level at 343°C, unlike that exhibited with the DTBP initiator at 316°C, although the decrease is very gradual.

EXAMPLE 4

Preparation of Styrene/Acrylic Comonomers

Several comonomers were prepared by polymerizing styrene in a reactor similar to that described in Figure 1 with either methylmethacrylate (MMA), acrylic acid (AA) or hydroxyethylmethacrylate (HEMA). In each case the monomer mixture consisted of 70 wt. % styrene and 30 wt. % co-monomer and the reaction temperature was varied between 316°C and 343°C. In addition, the initiator level (DTBP) was varied between 0 and 0.5 wt. %.

EXAMPLE 5

Preparation of Poly(butyl acrylate) Homomonomer

(Reaction Temp. 285°C)

N-Butyl acrylate (BA) was polymerized using the apparatus illustrated in Figure 2. First, 6000 g of BA (100 wt. parts) and 30 g DTBP (0.5 wt. parts) were added to the monomer feed tank. A solvent (Carbitol) was fed to the reactor from the solvent tank to fill the reactor. Next, the temperature of the reactor was elevated to 225°C and the pressure in the reactor was maintained at about 24 to 26 kg/cm² · G by means of a pressure controller. The monomer feed was then fed to the reactor at a rate of 22 g/min. The reactor was operated with a 13.6 minute average reactor residence time. The reaction temperature was maintained at about 285°C. The process was kept at a steady state condition for at least one hour before sampling. The number of terminal double bonds per chain (TDB/chain) was measured using ¹H NMR spectroscopy. The broad signal at δ=4 ppm was due to the methylene adjacent to the carboxyl oxygen, and the signals at δ=5.5 and δ=6.1 ppm were due to the terminal double bond. The ratio of the area due to the double bond and the area due to the methylene is multiplied by P_n to obtain TDB/chain. The temperature, the DTBP level, the number average molecular weight (M_n), the weight average molecular weight (M_w) (M_n and M_w were determined by Gel Permeation Chromatography), and the TDB/chain are set forth below in Table 6.

EXAMPLE 6

Preparation of Poly(butyl acrylate) Homomonomer

(Reaction Temp. 315°C)

A poly(butyl acrylate) homomacromer was prepared in a manner similar to Example 5, with the exception that the reaction temperature was about 315°C and the residence time was 12 minutes. The M_n , M_w and TDB/chain data are set forth in Table 6.

Table 6

Example	Temp (°C)	%DTBP	M_n	M_w	TDB/chain
5	285	0.5	1540	3000	0.71
6	315	0.5	1300	2570	0.95

5

EXAMPLE 7

Preparation of an Acrylic Comacromer

An acrylic comacromer was prepared in a manner substantially similar to that set forth in Example 6, with the exception that the 79.97 % w/w butyl acrylate, 19.99 % w/w acrylic acid and 0.04 % w/w DTBP were employed. The M_n , M_w and TDB/chain data for the

10 resulting comacromer are set forth in Table 7.

EXAMPLE 8

Preparation of an Acrylic Comacromer

An acrylic comacromer was prepared in a manner substantially similarly to that of Example 7, with the exception that the reaction temperature was 295°C. The M_n , M_w and TDB/chain

15 data for the resulting comacromer are set forth in Table 7.

Table 7

Example	Temp (°C)	DTBP (% w/w)	M_n	M_w	TDB/chain
7	315	0.04	1450	2920	0.85
8	295	0.04	1810	3790	0.97

EXAMPLE 9

Preparation of Acrylic Comacromer

A comacromer was prepared in a manner substantially similar to Example 5 by polymerizing 67.6 % w/w hexyl acrylate, 19.35 % w/w hydroxyethyl acrylate, and 9.7 % w/w hydroxyethyl methacrylate in the presence of 2.5 % w/w isopropyl alcohol and 1% w/w DTBP at a reaction temperature of 270°C for a 12 minute residence time. The M_n , M_w and TDB/chain data for the resulting comacromer are set forth in Table 8.

EXAMPLE 10

Preparation of Styrene Homomacromer in a Tube Reactor Styrene homomacromer were prepared in a tube reactor that consisted of a 1/16 inch (0.16 cm) outer diameter (OD) stainless steel tube immersed in a 600 ml pressure reactor filled with MAROLOTHERM™ SH (Huls) heat transfer oil. The 600 ml reactor was heated with an electric heating mantle. The oil was heated to the desired reaction temperature and the monomer subsequently pumped through the tube. The residence time was varied by changing the monomer feed rate or the length of the tube immersed in the oil or both.

The pressure in the tube was controlled at the desired setpoint by a pressure control valve at the tube outlet. In all cases the pressure was maintained in the tube reactor between about 550-600 psia (3792-4137 kPaa). The monomer feed was 100% styrene. The various reaction temperatures and residence times along with the M_n , M_w and DB/chain for the resulting styrene homomacromers is set forth in Table 8 below.

Table 8

Example	Temp. (°C)	Residence Time (min.)	M_n	M_w	DB/chain
9	270	12	1900	2920	0.75
10A	343	6.33	794	2640	1.1
10B	343	10.06	740	2600	1.2
10C	343	15.1	700	2675	1.2
10D	343	15.1	706	2710	0.9
10E	371	6.33	495	1285	1.1
10F	371	10.06	463	1190	1.0
10G	371	15.1	447	1205	0.8
10H	371	15.1	460	1290	0.9

EXAMPLE 11

(A) Preparation of Terminally Unsaturated Hydroxyethyl Methacrylate/Styrene Comacromer

A mixture of styrene (99.0% w/w) and 2-hydroxyethyl methacrylate (HEMA) (1.0% w/w) was fed into an empty 10 gallon (37.9 liter) stainless steel reactor with agitation and the reactor jacket was set at 321°C. The mixture was fed at a rate of 3 lbs/min. (1.36 kg/min.) until 46 lbs (20.9 kg) had been added, at which point the reactor bottom was opened to allow the product out of the reactor at a rate which maintained a constant level of polymerizable reactant in the reactor resulting in a 15 minute residence time. The comacromer was continuously fed to a wiped film evaporator having a temperature of 263°C and under a pressure of 4.9 psia (33.8 kPaa). The resulting comacromer product was then pumped out of the evaporator and collected.

(B) Use of the HEMA/Styrene Comacromer As a Reactive Substrate for Reaction with Acrylic Acid

(i) A 50/50 (wt) mixture of HEMA/styrene comacromer prepared above and toluene was prepared. Approximately 40.75 lbs (18.5 kg) of this mixture was pumped into the reactor described above. The reactor was heated to 165°C and 9.2 lbs (4.2 kg) of a mixture of acrylic acid (96.75% w/w) and DTBP (3.25% w/w) was fed to the reactor at a rate of 0.308 lbs/min (0.14 kg/min.). The reactor temperature was raised to 260°C and held for 60 minutes. The polymerized mixture was then pumped to a wiped film evaporator set at 232°C and approximately 5-8 psia (34.5-55.2 kPaa) at a rate of approximately 2.5 lbs/min (1.13 kg/min.) The resulting acrylic grafted comacromer was pumped out of the evaporator and collected. The acid number, percent acrylic acid (AA) conversion, M_n , M_w and polydispersity (Pd) are set forth in Table 9.

(ii) A 50/50 (wt) mixture of the HEMA/styrene comonomer prepared above and toluene was added to the reactor (42 lbs/19.1 kg). The reactor was heated to 165°C and 8.9 lbs (4 kg) of a mixture of acrylic acid (96.85% w/w) and DTBP (3.15% w/w) was fed to the reactor at a rate of 0.29 lbs/min (0.13 kg/min.). The reactor temperature was raised to 200°C and held for 60 minutes. The polymerized mixture was then pumped to the film evaporator under the same conditions described above and the acrylic grafted comonomer collected. The acid number, percent acrylic acid conversion, M_n , M_w , and Pd are set forth in Table 9.

(iii) The grafted comonomer produced in Example 11(B)(i) (10 lbs/4.5 kg) and the comonomer produced in Example 11(A) (20 lbs/9.1 kg) was added to the 10 gallon (37.9 liter) reactor described above. The reactor was heated to 176°C to melt the components and then the temperature was reduced to 165°C. Next, 17.5 lbs (7.9 kg) of a mixture of acrylic acid (49.2% w/w), acetone (49.2% w/w) and DTBP (1.6% w/w) was fed to the reactor at a rate of 0.58 lbs/min (0.26 kg/min.). This was followed by the addition of 7.28 lbs (3.3 kg) of acetone to the reactor to maintain an open feed line. The reactor was then heated to 200°C and held for 60 minutes. The polymerized mixture was then pumped to the film evaporator under the conditions described above and the grafted comonomer product was collected. The acid number, percent acrylic acid conversion, M_n , M_w , and Pd are set forth in Table 9.

Table 9

Example	Acid #	AA Conversion	M_n	M_w	Pd
11B(i)	113	98%	940	1505	1.67
11B(ii)	67.4	73.4%	1130	1900	1.69
11B(iii)	143.6	78.9%	1375	2745	2.0

(C) Use of the Grafted Comacromer as a Surfactant in an Emulsion Polymerization Preparation of Styrene Homomacromer in a Tube Reactor Styrene homomacromer were prepared in a tube reactor that consisted of a 1/16 inch (0.16 cm) outer diameter (OD) stainless steel tube immersed in a 600 ml pressure reactor filled with MAROLOTHERM™ SH (Huls) heat transfer oil. The 600 ml reactor was heated with an electric heating mantle. The oil was heated to the desired reaction temperature and the monomer subsequently pumped through the tube. The residence time was varied by changing the monomer feed rate or the length of the tube immersed in the oil or both.

10 A resin solution was prepared by adding 420g of the graft comacromer (11B(iii)) to 1000g of deionized water with agitation. Next, 70g of ammonia (28%) was added. This mixture was heated to 85°C and mixed for 30 minutes to dissolve the resin. Then 301.3g of the resin solution and 93.8g of deionized water were added to a 1 liter flask fitted with paddle agitators and a heating mantle. This mixture was heated to 15 82°C with agitation. Next, 7.64g of a 20% ammonia persulfate solution in water was added and the reactor contents held for 10 minutes. This was followed by the addition of 118.8g of styrene at a constant rate over 35 minutes while maintaining the reactor temperature at 82°C. The emulsion polymerized mixture was then held for 60 minutes at 82°C. The resulting emulsion polymer had a number average 20 particle size of 48 nanometers and a weight average particle size of 75 nanometers. The emulsion viscosity was 1690 cps (1.69 pascal-seconds) with a solids level of 39.76% and a pH of 8.36. Other variations and modifications of this invention will be obvious to those skilled in the art. This invention is not limited except as set forth in the claims.

WHAT I CLAIM:

1. A process for preparing low molecular weight homomacromers, said process comprising the steps of:
 - 5 (a) charging a reactor with (i) a single ethylenically unsaturated monomer selected from the group consisting of acrylic monomers or monoalkenyl aromatic monomers and (ii) if said ethylenically unsaturated monomer is not a thermally initiating monomer, a free radical polymerizable initiator, to form a polymerizable reaction charge; and
 - (b) heating the reaction charge during continuous mixing in the reactor to a reaction
10 temperature in the range from about 180°C to about 500°C for a residence time greater than 5 minutes to form the low molecular weight homomacromers,
provided that if the residence time is 60 minutes or less that the reaction temperature is greater than 270°C.
2. The process of claim 1, wherein the reactor is a continuous stirred tank reactor, a
15 continuous loop reactor or a tube reactor.
3. The process of claim 2, wherein the reaction charge is comprised of the acrylic monomer.
4. The process of claim 3, wherein the acrylic monomer is an acrylate or methacrylate.
5. The process of claim 3, wherein the residence time is from about 10 minutes to about 60
20 minutes.
6. The process of claim 5, wherein the reaction temperature is in a range from about 275°C to about 400°C.
7. The process of claim 5, wherein the acrylic monomer is selected from the group consisting of n-butyl acrylate, acrylic acid, methacrylic acid, methyl acrylate, isopropyl
25 acrylate, methyl methacrylate, hexyl acrylate, hydroxyethyl acrylate and hydroxyethyl methacrylate.
8. The process of claim 1, wherein said reaction charge comprises up to about 3 wt. % of the free radical polymerization initiator based on total weight of ethylenically unsaturated monomer.
- 30 9. The process of claim 2, wherein the reaction charge comprises the monoalkenyl aromatic monomer.
10. The process of claim 9, wherein the monoalkenyl aromatic monomer is selected from the group consisting of styrene or alpha-methylstyrene.

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11. The process of claim 10, wherein the residence time is from about 10 minutes to about 120 minutes.
12. The process of claim 11, wherein the reaction temperature is in the range from about 275°C to about 400°C.
- 5 13. The process of claim 12, wherein said reaction charge comprises up to about 3 wt. % of the free radical polymerization initiator based on total weight of ethylenically unsaturated monomer.
14. The process of claim 9, wherein the residence time is from about 10 minutes to about 45 minutes.
- 10 15. The process of claim 14, wherein the reaction temperature is in the range from about 315°C to about 400°C.
16. A process for preparing low molecular weight comonomers, said process comprising the steps of:
- (a) charging a reactor with (i) at least two ethylenically unsaturated monomers
15 selected from the group consisting of acrylic monomers, monoalkenyl aromatic monomers or mixtures thereof and (ii) if at least one of said ethylenically unsaturated monomers is not a thermally initiating monomer, a free radical polymerization initiator, to form a polymerizable reaction charge; and
- (b) heating the reaction charge during continuous mixing in the reactor to a reaction
20 temperature in the range from about 180°C to about 500°C for a residence time greater than 5 minutes to form the low molecular weight comonomers,
- provided that if the residence time is 60 minutes or less that the reaction temperature is greater than 270°C and further provided that if the reaction charge is a mixture of acrylic monomer and monoalkenyl monomer and the residence time is 60 minutes or less then the
25 reaction temperature is greater than 310°C.
17. The process of claim 16, wherein the reactor is a continuous stirred tank reactor, a continuous loop reactor or a tube reactor.
18. The process of claim 17, wherein the reaction charge is comprised of a mixture of the acrylic monomer.

19. The process of claim 18, wherein the acrylic monomers are selected from acrylates, methacrylates or mixture thereof.
20. The process of claim 18, wherein said reaction charge further comprises at least one monoalkenyl aromatic monomer.
- 5 21. The process or claim 20, wherein the monoalkenyl aromatic monomer is selected from the group consisting of styrene or alpha-methylstyrene.
22. The process of claim 17, wherein said reaction charge is a mixture of at least one acrylic monomer and at least one monoalkenyl aromatic monomer.
23. The process of claim 22, wherein said acrylic monomer is an acrylate or
10 methacrylate.
24. The process of claim 22, wherein the acrylic monomers are selected from the group consisting of n-butyl acrylate, acrylic acid, methacrylic acid, methyl acrylate, isopropyl acrylate, methyl methacrylate, hexyl acrylate, hydroxyethyl acrylate and hydroxyethyl methacrylate.
- 15 25. The process of claim 23, wherein said monoalkenyl aromatic monomer is selected from the group consisting of styrene or alpha-methylstyrene.
26. The process of any of claims 18-25, wherein the residence time is from about 10 minutes to about 120 minutes.
27. The process of claim 26, wherein the reaction temperature is in the range from about
20 315°C to 400°C.
28. The process of claim 27, wherein the residence time is from about 10 minutes to about 45 minutes.
29. The process of claim 16, wherein said reaction charge comprises up to about 3 wt. % of the free radical polymerization initiator based on total weight of ethylenically unsaturated
25 monomer.

FIG. 1

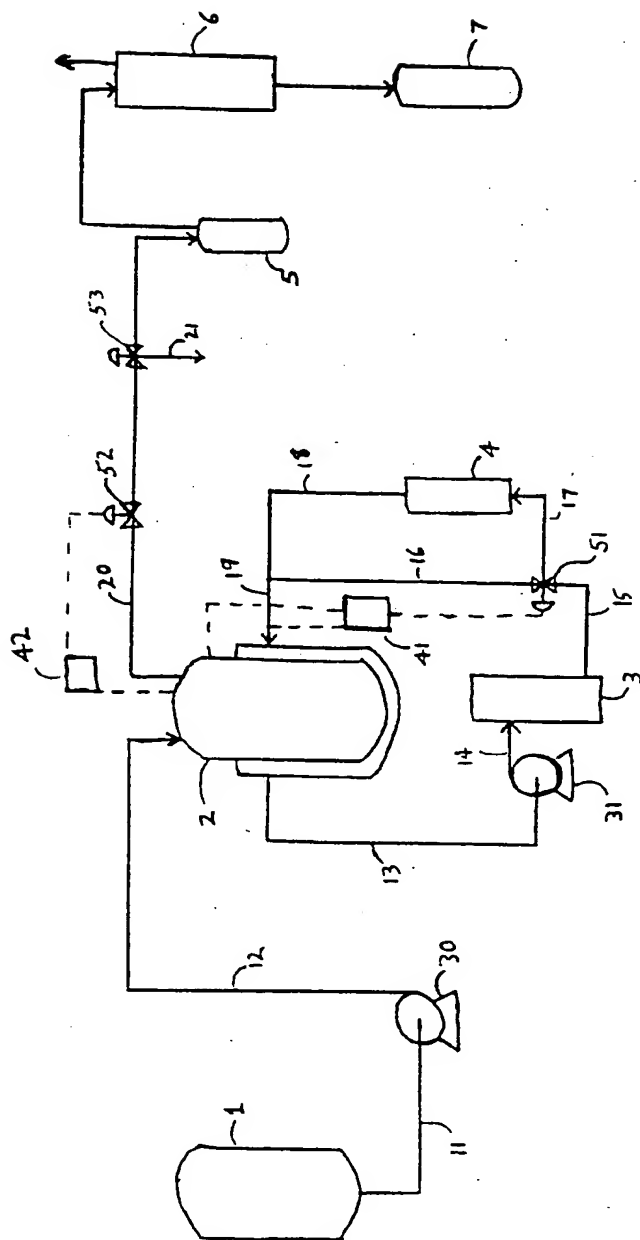
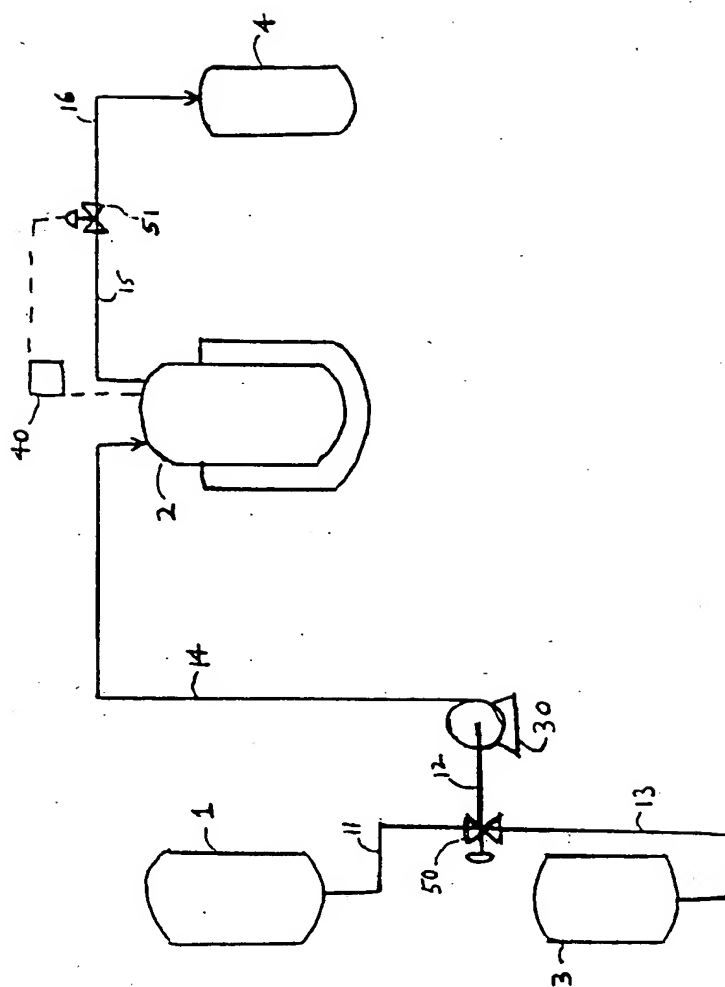


FIG. 2



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(21) International Application Number: PCT/US98/16198 (22) International Filing Date: 4 August 1998 (04.08.98) (30) Priority Data: 08/906,141 5 August 1997 (05.08.97) US (71) Applicant: SC JOHNSON COMMERCIAL MARKETS, INC. [US/US]; 8310 16th Street, P.O. Box 902, Sturtevant, WI 53177-0902 (US). (72) Inventors: CAMPBELL, J., David; 713 Silent Sunday Court, Racine, WI 53402 (US). KAAI, Michihiro; Toyoake-shi, 1187-81, Tsurune Magome-cho, Toyoake-shi 470-11 (JP). SCHATZ, David, D.; 2931 Washington Avenue, Racine, WI 53405 (US). TEYMOUR, Fouad; 1825 West Palm Drive, Mt. Prospect, IL 60056 (US). (74) Agents: RYMARZ, Renee, J. et al.; SC Johnson Commercial Markets, Inc., Patent Section, 8310 16th Street M/S 510, Sturtevant, WI 53177-0902 (US).		(81) Designated States: AU, CA, CN, JP, KR, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 24 June 1999 (24.06.99)
(54) Title: PROCESS FOR THE PREPARATION OF MACROMERS		
(57) Abstract <p>A process is disclosed for preparing low molecular weight homomacromers and comacromers. The process of preparing a homomacromer comprises the steps of: (a) charging a reactor with (i) a single ethylenically unsaturated monomer selected from the group consisting of acrylic monomers or monoalkenyl aromatic monomers and (ii) if said ethylenically unsaturated monomer is not a thermally initiating monomer, a free radical polymerizable initiator, to form a polymerizable reaction charge; and (b) heating the reaction charge during continuous mixing in the reactor to a reaction temperature in the range from about 180 °C to about 500 °C for a residence time greater than 5 minutes to form the low molecular weight homomacromers, provided that if the residence time is 60 minutes or less that the reaction temperature is greater than 270 °C. The comacromers are prepared by charging the reactor with (i) at least two ethylenically unsaturated monomers selected from the group consisting of acrylic monomers, monoalkenyl aromatic monomers or mixtures thereof and (ii) if at least one of said ethylenically unsaturated monomers is not a thermally initiating monomer, a free radical polymerization initiator, and heating the reactor to a reactor temperature in the range from about 180 °C to about 500 °C for a residence time greater than 5 minutes to form the low molecular weight comacromers, provided that if the residence time is 60 minutes or less that the reaction temperature is greater than 270 °C and further provided that if the reaction charge is a mixture of acrylic monomer and monoalkenyl monomer and the residence time is 60 minutes or less then the reaction temperature is greater than 310 °C.</p>		

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INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO 96 33224 A (E.I. DU PONT DE NEMOURS AND CO.) 24 October 1996 cited in the application -----	

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Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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